

9/786126

PTO/PCT Rec'd 01 FEB 2001

SEMICONDUCTOR GAS SENSING

This invention relates to the semiconductor gas sensing of oxidising gases such as nitrous and nitric oxide, chlorine, and ozone.

In the following description the invention will be exemplified with reference to ozone sensing, but the general principles are applicable to other oxidising gases. Parts per billion (ppb) quoted hereinafter are by volume.

In our previous application WO-95/35495, we described a method of measurement of ozone concentration involving the measurement of electrical resistance of a porous tungstic oxide element, held at elevated temperature (200-500°C). When the element is held at constant temperature, the sensitivity to ozone tends to vary with time and to be dependent upon the history of the device, including previous exposure to ozone. Other semiconducting oxides have been shown to exhibit resistance increases at elevated temperature in the presence of small concentrations of ozone in the air: In_2O_3 , pure and variously doped, by Takada et al, Sensors & Actuators B : Chemical 13 (1993) 404; MoO_3 by Garlo et al., Sensors & Actuators B : Chemical 47 (1998) 92. We have now discovered that SnO_2 also shows the effect (see Figure 1), though at rather lower temperature (~200°C) and with problems of baseline stability. We believe that the phenomenon is generic to a certain general class of semiconducting oxides for which oxygen vacancies can be created at the surface, at the operating temperature, in air, in sufficient concentration to substantially affect the concentration of electronic charge carriers and hence the electrical conductivity.

The invention is defined by the claims hereinafter.

We have discovered a method for analysis of ozone concentration in air, which is generally applicable to the afore-mentioned class of oxides.

The method surprisingly results in (1) a significant increase in the stability of the signals generated by sensors incorporating these materials, and (2) significantly reduces the lower detection limit of the sensors for ozone to concentrations of a

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few ppb, which is typical of the UV ozone analysers conventionally employed to detect this molecule. The method involves causing a perturbation of the temperature of the sensor and analysing the resulting time variation of the sensor resistance or conductance.

The method gives substantially increased accuracy and stability, and consequently a greater reliability of measurement, especially at very low ozone concentration (less than 100 ppb in air). A very low detection limit for ozone can be achieved, which can be reliably sustained in measurement over a long period of time. A typical detection limit achieved using a device based on WO_3 is 2.5 ppb in air, reliably sustained without change of calibration over at least 3 months.

Preferred features of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the response of an SnO_2 sensor operated at 175°C to a pulse of 50 ppb ozone in air,

Figure 2 is a graph showing the response of a WO_3 sensor to 50 ppb ozone in air after having been stepped to 600°C from an operating temperature of 400°C ,

Figures 3 and 4 show the variations in time constants of equation (1) hereinafter with ozone concentration,

Figure 5 shows the variation in resistance of the WO_3 sensor to ozone concentration and the result of curve fitting applied thereto,

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Figure 6 shows the response of the WO_3 sensor to ozone concentration over a period of days,

Figure 7 is a graph illustrating the time required to reset the sensor surface as a function of reset temperature,

5 Figure 8 is a graph illustrating the energy consumed in resetting the sensor surface, as a function of reset temperature,

Figure 9 compares the results of employing a WO_3 sensor according to the invention to monitor street level ozone concentration as compared to similar results obtained with a conventional UV absorption instrument, and

10 Figure 10 compares the results of employing a WO_3 sensor according to the invention to provide a vertical profile of ozone in the atmosphere as compared to similar results obtained with a conventional instrument,

The invention involves perturbing the sensor as follows:

- 20
- step to a high temperature to reset the surface
 - step back to a low temperature to make the measurement
 - analyse the variation of resistance with time at the low temperature to obtain the ozone concentration
 - repeat the sequence.

25 For example with a device based on WO_3 , the "high" temperature can be 400°C - 800°C and the "low" temperature can be 200°C - 500°C , with the obvious constraint that the "high" temperature should be greater than the "low" temperature.

Figure 2 shows an example of this. In the presence of ozone in the air,

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the device temperature was stepped to 600°C for 300s, then stepped back to 400°C for 300s. The time-variation of resistance at 400°C following the step back ($t=0$) is shown. The conductivity, S (reciprocal of resistance) at the low temperature shows the following variation:

$$S(t) = S_{lim} + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where

$$S_{lim} = S_{\infty} + b_0/(O_3)$$

$$\tau_1 = b_1/(O_3)$$

$$\tau_2 = b_2/(O_3)$$

where (O_3) denotes the ozone concentration.

Here, S_{∞} , a_j are constants which depend on the time and temperature of the "high" temperature step. The b_j depend upon the temperature of the "low" temperature step, at which the measurement is made but do not depend on the high temperature step values. Typically, $b_2 \approx 10b_1$, so that the second time-dependent term is only significant at higher ozone concentration. If the measurement temperature (the "low" temperature) is decreased then the ratio b_2/b_1 increases, so again the second time-dependent term becomes less significant.

Application of method to ozone measurement

(a) by curve-fitting the data to equation (1), the values of τ_1 , τ_2 are determined. By reference to a calibration curve of τ_1 (and if necessary τ_2) against ozone concentration, the ozone concentration is obtained. The sensor and the stability of the operating circuitry are checked by checking the stability of the parameters S_{∞} , a_1 , a_2 , which are also obtained from the fit. If the measurement time is limited, or the ozone concentration is low enough, or the measurement temperature is low enough, then only one time constant will be required to describe the data, and the reliability of the parameter fit can be improved.

In the example shown in Figure 2, the fitted curve provided the values τ_1

= 30s (seconds) and τ_2 - 130s. Examples of the variation of time constants with ozone concentration are shown in Figures 3 and 4. In Figure 4, the fitted line corresponded to

$$\tau/s = (1300 \pm 70)/(O_3 \text{ppb})$$

5 Figure 5 shows the variation of sensor resistance to ozone concentration and fitting the equation

$$1/R = a + b/O_3$$

to the results. In the example shown

$$a = 1.81 \cdot 10^{-7} \Omega^{-1}$$

10
$$b = 2.44 \cdot 10^{-5} \Omega^{-1} \cdot \text{ppb}$$

(b) the resistance or conductance at a particular time after the change of temperature can be determined, and the ozone concentration can be obtained from a calibration curve of this resistance against ozone concentration.

Manipulation of equation (1) shows that a linear calibration of either
15 conductance or resistance will be obtained if the time constants τ_1, τ_2 are sufficiently long: i.e. at low $[O_3]$. Figure 6 shows an example. In this example, between the calibration runs, the sensor had been used continuously, measuring ozone in urban air. The calibration did not drift over a period of some months. From the calibration line, a detection limit of 2.5 ppb is deduced.

20 In Figure 6, the ordinate "Response" is $R_g/R_o - 1$, where R_g is the resistance of the sensor in the presence of ozone and R_o is the resistance in the presence of air. The response values were taken at 128s, with all data having a relative humidity of 49%. The data can be fitted to a straight line

$$\text{Response} = A + B \cdot [O_3]$$

25 In the example shown in Figure 6

$$A = -0.192 \text{ with a standard deviation of } 0.083$$

$$B = 0.045 \text{ with a standard deviation of } 0.002.$$

Unlike (a), this method requires the parameters S_∞, a_1, a_2 to remain stable that is, that the surface should be fully "reset". We have found that this

can be achieved by an appropriate choice of temperature and time for the "high" temperature step. For Figure 6, it was 600°C and 300s, with measurement at 400°C. Figure 7 shows the required time (for reset) as a function of the temperature, for WO₃-based devices. The higher the temperature, the shorter the time. Figure 8 shows the energy consumption during the high temperature step (power required x time required). The energy consumption decreases with increasing reset temperature. So, the higher the reset temperature the better, both for time resolution (the device is not measuring during the reset period) and for energy consumption (the less energy consumed the better for applications requiring battery power, e.g. balloon-borne instruments).

(c) the time, t^* required to achieve a particular resistance, R^* , can be measured and the ozone concentration derived from a calibration derived from a calibration curve. From equation (1), t^* varies approximately as $1/(O_3)$. The value, R^* , is chosen according to the expected ozone concentration: obviously, choosing a lower value will decrease t^* for a given (O_3). This method has the advantage of measurement simplicity: a counter is started at the end of the reset pulse and stopped when a comparator circuit senses that the measuring current through the sensor falls below a preset level.

(d) is a combination of (b) and (c). The resistance is monitored as a function of time until the end of a preset measurement time, t_m . A resistance trigger level, R^* , is also set. If, during t_m , the resistance exceeds R^* , then the time of this occurrence, t^* , determines the ozone concentration, the sensor is reset and the sequence repeats. If, at the end of t_m , $R_m < R^*$, then the value of resistance R_m at t_m is used to determine the ozone concentration, the sensor is reset and the sequence repeats. This method gives a wide dynamic range and good response time with simple electronics.

The validity of the results of the two step temperature technique are shown in Figures 9 and 10. In Figure 9 the variation in street level ozone concentration over a period of four days was measured with a WO₃ sensor as

well as with a conventional UV absorption instrument. The two types of measurements agree generally quite well.

Figure 10 shows the results of vertical profiling for ozone in the atmosphere using a WO_3 sensor given a single high temperature reset pulse, and the equivalent results from a conventional ECC ozone sonde. Again, the results agree generally well.

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Now, consider the resistance oscillation due to the presence of ozone, for the case of a square-wave oscillation of temperature. Equation (1) gives the conductance as a function of time at each of the two temperatures. Because, in this method, the sensor surface is not periodically being completely reset by a step to high temperature, the parameters S_{∞} and a_i may vary with time, dependent on the history of the device and the ozone concentration. However, the parameters b_i do not so vary. Thus the time constants τ_i depend only on the temperature and on the ozone concentration. The method therefore comprises the following steps:

- (1) subtracting the instantaneous change of resistance following each temperature step
- (2) determining the amplitude of the remaining temperature oscillation, from which the ozone concentration may be determined, by reference to a calibration curve
- (3) determining the time constants for each of the two temperatures, according to equation (1), either by curve-fitting equation (1) or by calculation from the resistance values at two or more times during each period of constant temperature
- (4) deriving two further estimate of ozone concentration by reference to calibration curves for the two temperatures.

The method may be generalised to other waveforms for the temperature perturbation, e.g. sinusoidal, using the process of first filtering to remove the instantaneous resistance change caused by the change of temperature and then harmonic analysis, time-correlation function calculation or Fourier transformation to obtain the amplitudes and time constants associated with the ozone-dependent signal, then comparison with calibration curves to derive the ozone concentration.

Method 3 - switch the air stream periodically through a suitable ozone decomposition catalyst

- analyse the resistance variation of the sensor when the ozone is reapplied.

This method is simple to implement using switching valves.

5 The sensor signal when the ozone-destruction catalyst is switched out of the air stream follows equation (1). Figure 11 shows a typical response to a sequence of two pulses of ozone interspersed with ozone-free air, with a number of sensors at constant temperature. The increase of signal amplitude with total ozone dose is a characteristic of these devices when measured at constant temperature, as is the variation between devices. However, the time
10 variation of the signal can be fitted to equation (1). The time constants so derived do not vary from one pulse to another, or from one device to another, wherein reasonable experimental error and the ozone concentration can be determined from the time constants, by reference to a calibration curve. As with the temperature-switching method, this method does not require the sensor
15 resistance to stabilise in order that the ozone concentration be accurately determined.

The results from Figure 11 were for a number of WO_3 sensors powered for 5 days at 400, 500 and 600°C, left unpowered for 30 minutes, and then the two pulses of ozone (50 ppb) applied with measurement made at 500°C. The
20 results from Figure 11 gave time constants $\tau_1 = 77 \pm 21\text{s}$ and $\tau_2 = 520 \pm 61\text{s}$.

Method 4 - periodically greatly reduce the airflow rate over the sensor, then increase it again, with the sensor at constant temperature.
- analyse the time variation of the signal following the increase of flow rate.

25 This method works because ozone is decomposed within the thermal boundary layer near the sensor. The variation of signal with airflow rate normal to the sensor is shown in Figure 12. In Figure 12, the results are for a WO_3 sensor at 400°C exposed to 50 ppb ozone. As for flow rate, 1 Lmin^{-1} equates to about 20 cm.s^{-1} flow velocity normal to the sensor. At sufficiently high flow rate,

the signal achieves a plateau, because ozone is transported to the surface at a rate sufficiently greater than the rate of thermal decomposition near the sensor. At lower flow rate, the signal falls reflecting the fall in ozone concentration near the sensor. At low enough flow rate, the sensor signal is virtually zero.

5 Therefore, if the air flow to the sensor is greatly reduced, (cutting off the flow completely is, of course, one option) then the sensor resistance will relax towards the value characteristic of a zero ozone concentration. Just as in method 3, it is not necessary to attain an exact zero, however. When the flow rate is increased again, to a value on the plateau of Figure 12, the sensor
10 resistance will increase with time, following equation (1). Curve-fitting equation (1), or calculation from two or more points gives the time constants. By reference to a calibration curve, the time constants give the ozone concentration. The other parameters of equation (1) can be used to diagnose continued reliable operation of the sensor.

15 The power drawn by the sensor device will depend on the air flow rate. Therefore, monitoring the sensor power consumption serves two purposes:

(a) it checks that the required flow rate is indeed being delivered and hence diagnoses failure of any of the other components of the system or blockage of the pipe work;

20 (b) it provides a trigger signal to actuate the resistance measurement circuits at the correct time, thus compensating for delays in the flow lines.